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Elimination of overlapping orders in X-ray absorption spectra

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With 2 figures in the text

In studies of X-ray absorption spectra the accelerating voltage of the tube is usually kept lower than twice the excitation potential of the first order continuous radiation. In this way the distortion by overlapping orders is avoided. At comparatively long wave-lengths, however, difficulties often arise if this rule is strictly followed and the accelerating voltage has thus to be correspondingly low. Not only does the intensity of the first order continuous spectrum decrease, but special arrangements have to be made for the focussing of the cathode ray beam. It follows that registration with counters demands extended counting periods if the statistical fluctuations are to be kept within acceptable limits. This is a serious drawback as the probability of changes in the target as well as in the absorber will increase with the time of irradiation.

This problem of conflicting interests would be solved easily if a selective absorption of the second and following orders could be arranged, but such an arrangement would have a destructive influence on the intensity of the first order. On the contrary, while working with a comparatively high accelerating voltage it is sometimes possible to determine the intensity component arising from overlapping orders. For this purpose an additional set of measurements has to be collected, a thick absorber removing the first order almost completely, at least in some part of the spectrum. In practice, for reasons of accuracy it will prove impossible to cope with more than two orders.

Let I_{I}, I_{II}, etc. be the intensities of the components of the first and following orders and I_0 the total intensity of the unfiltered radiation. Let I_1 be the intensity of the radiation filtered through an absorber of thickness a_1 and having the unknown absorption coefficient $\varkappa_x$ in the first order. Suppose also that the absorption coefficients $\varkappa_{\mathrm{II}}$, $\varkappa_{\mathrm{III}}$, etc. for the folloving orders have been determined previously. Let I_2 be the intensity of the radiation filtered through the second absorber having the absorption coefficients $\varkappa_1$, $\varkappa_2$, etc. The thickness a_2 of this second absorber is assumed to suffice for the exclusion of the first order spectrum as compared to other sources of errors. I_0, I_1, and I_2 being measured, $\varkappa_x$ will be found from the equations

$$I_0 = I_{\mathrm{I}} + I_{\mathrm{II}} + I_{\mathrm{III}} + \cdots, \tag{1}$$

$$I_1 = I_{\mathrm{I}} e^{-\varkappa_x a_1} + I_{\mathrm{II}} e^{-\varkappa_{\mathrm{II}} a_1} + I_{\mathrm{III}} e^{-\varkappa_{\mathrm{III}} a_1} + \cdots, \tag{2}$$

$$I_2 = I_{\mathrm{II}} e^{-\varkappa_1 a_2} + I_{\mathrm{III}} e^{-\varkappa_2 a_2} + \cdots. \tag{3}$$

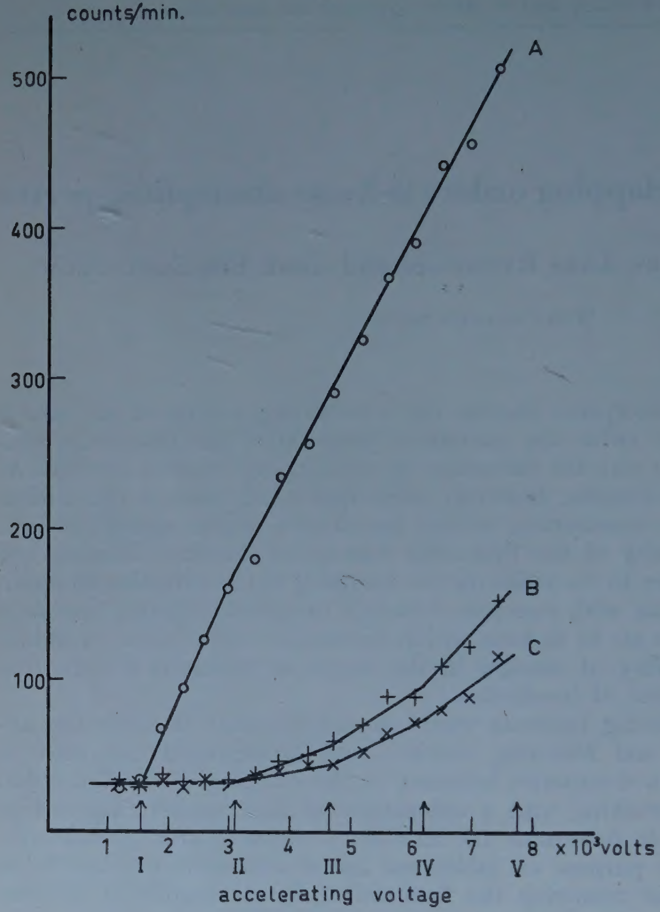

Fig. 1. The relative intensity of the continuous X-ray spectrum as a function of the accelerating voltage for (A) the unfiltered radiation, (B) the radiation through 3.9 μ Al, and (C) filtered through 7.0 μ Al. The arrows on the abscissa axis mark the excitation voltages of the orders indicated by Roman figures.

In the normal case the intensity I_{III} of the third order will be negligible and all further orders lacking.

It has to be remembered that the counting rate in each order is a function not only of the accelerating voltage but also of the coefficient of reflexion of the crystal and the spectral sensitivity of the detector.

Naturally the numbers of counts corresponding to I_0, I_1, and I_2 have to be so large as to make the statistical fluctuations of the differences $I_0 - I_2 e^{\varkappa_2 a_2}$ and $I_1 - I_2 e^{\varkappa_2 a_2 - \varkappa_{\mathrm{II}} a_1}$ as low as is practically possible. An additional error is introduced, nevertheless, through the difficulty of determining accurately the effective thickness a_2 of the second absorber.

If only a narrow wave-length region is to be investigated, an average value of $\varkappa_2$ can be used throughout this region without introducing any serious errors.

Before starting absorption measurements a rough survey ought to be made regarding the properties of the radiation as a function of the accelerating voltage. As a preliminary study the first three orders of the radiation from a tungsten

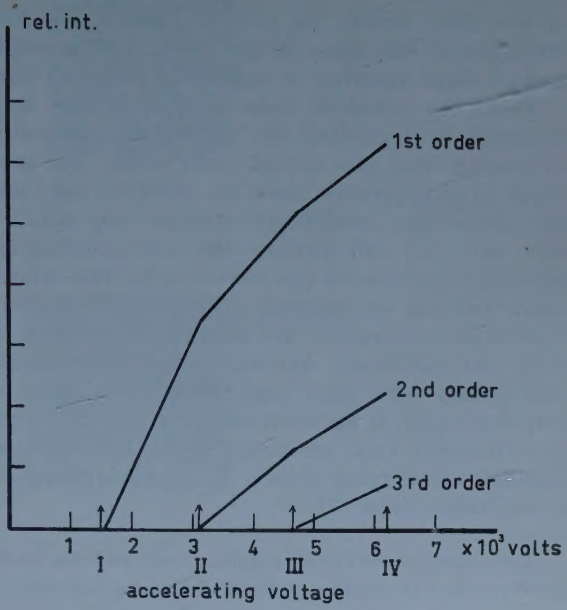

Fig. 2. Relative intensities of the separated first three orders continuous spectra as a function of the accelerating voltage. The arrows on the abscissa axis mark the excitation voltages of the orders indicated by Roman figures.

target were separated at a wave-length of 7910 XU by means of two Al-foils, 3.9 and 7.0 microns thick.

The instrumental equipment consisted of a bent crystal spectrometer [1] with an X-ray tube [2] both previously described. The crystal was quartz with the plane-system $(10\bar{1}0)$.

As the measurements were made on the short wave-length side of the Al K-edge the employed absorbers were both able to remove the first order spectrum as is clearly indicated by the curves B and C in Fig. 1. Curve A illustrates the unfiltered radiation as a function of the accelerating voltage. As only a rough survey was intended no endeavour was made to attain a high statistical precision. Smooth curves can be drawn through the points of measurement although in some cases a discontinuous increase of the angular coefficient is indicated at the excitation voltages of the individual orders.

The separation of the first three orders follows from eqs. (1) and (3), the latter yielding one equation for each one of the two absorbers. To eliminate at least part of the accidental fluctuations the values of I_0, I_1 and I_2 were taken from the curves in Fig. 1 instead of from the individual measurements. The curves of the separated orders are reproduced in Fig. 2. No separation of the fourth order is possible, as measurements from two absorbers, only, are available.

It is important to note that the increase of the first order intensity is diminished each time a new order starts being emitted. Thus a point is eventually reached above which very little will be gained by a further increase of the accelerating voltage. The position of this point will certainly vary with the coefficient of reflexion as well as the voltage range. The present case is advantageous, the reflective power in the first order of the $(10\bar{1}0)$ planes of quartz increasing very fast with the glancing angle. Nevertheless Fig. 2 indicates that there is very little reason for employing an accelerating voltage above the excitation voltage of the third order, the step to that of the fourth order offering an increase in intensity of less than 20 per cent. This is emphasized by the trouble involved in using a third absorber as well as by the unavoidable decrease of accuracy.

From the available data it appears that an error of 8 per cent would be introduced by regarding the sum of the intensities of the second and third orders as arising from the second order solely, the accelerating voltage being 6 kV. This leads to the question how an error in the correction affects the results. In case the absorption coefficient exhibits only small variations with the wave-length, such an error will displace the corresponding curve with approximately the same amount regardless of the wave-length. The relative values of the absorption coefficient will not be seriously affected. Otherwise, if the variations are large, parts with a low absorption will scarcely be affected at all while those with a big coefficient are displaced. Actually, edges representing a big difference in absorption will appear with their high absorption region displaced relative to their low absorption region if the correction for the overlapping second order is not made with a sufficiently high accuracy. Nevertheless, the method outlined here might prove valuable in studying certain X-ray absorption spectra. An application will be given in a future paper [3].

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